Journal of Statistical Physics, Vol. 52, Nos. 5/6, 1988

Coincidence Theorem for the Direct Correlation Function of Hard-Particle Fluids

M. S. Wertheim[1]

Received March 25, 1988

The Mayer f-function for purely hard particles of arbitrary shape satisfies $f^2(1, 2) = -f(1, 2)$. This relation can be introduced into the graphical expansion of the direct correlation function $c(1, 2)$ to obtain a graphical expression for the case of exact coincidence, in position and orientation, of two identical hard cores. The resulting expression for $c(1, 1) + 1$ contains only graphs G from $c(1)$, the sum of irreducible graphs with one labeled point. Relative to its coefficient in $c(1)$, G occurs in $c(1, 1)$ with an additional factor R_c, which is 1 for the leading graph in the expansion and of the form $2 - 2L(G)$ for all other graphs. Here $L(G) = 0, 1, 2, \ldots$, is a nonnegative integer. Topological analysis is used to derive an expression for $L(G)$ in terms of the connectivity properties of G.

KEY WORDS: Hard-particle fluids; direct correlation function; graphs; connected; irreducible graphs; coincidence of hard cores.

1. INTRODUCTION

The idea of using hard spheres to model physical systems is very old, with notable calculations carried out in the late 19th century by Boltzmann.(1) In the 1950s computer simulations provided the first quantitative results for the equation of state of a hard-sphere fluid.(2,3) Soon afterward, the remarkably successful scaled particle theory (SPT) of Reiss *et al.*(4) gave rather good agreement with the simulation pressures over an extended density range. The idea of the SPT, slightly rephrased, is consideration of the configurational chemical potential $\Delta\mu$ of insertion of a hard sphere of arbitrary radius R into the fluid. The calculable limits of $R = 0$, R equal to the radius of a fluid particle, and R macroscopic provide benchmarks for interpolation. This work was further refined and applied by Reiss and

---

[1] Mathematics Department, Rutgers University, New Brunswick, New Jersey 08903.

0022-4715/88/0900-1367$06.00/0

co-workers.(5–8) A number of generalizations of the SPT to nonspherical hard particles have been proposed.(9,10)

Another approach to the equation of state is the calculation of the configurational Helmholtz free energy ΔA, and thus also $\Delta\mu$, by evaluation of the low-order cluster integrals by analytic, numerical, and Monte Carlo (MC) integration techniques (see Kilpatrick(11) for references). For hard spheres, these techniques, aided by the reformulation of the graphical expansion in terms of Ree–Hoover graphs(12–14) or overlap graphs(15) have provided good equations of state when used in the Padé approximant form.(12,14) Recently the MC integration has been applied to hard spheroids.(16)

A third approach is the one of integral equations for pair distributions, notably the Percus–Yevick(17) (PY) and hypernetted chain(18–23) (HNC) equations. For hard spheres there are analytic solutions of the PY equation(24,25) and numerical solutions of the HNC equation.(26) For nonspherical hard particles the numerical solution of these equations is difficult. Recently such solutions of the PY and HNC equations for prolate spheroids have been obtained by Perera *et al.*(27) who compared the results to MC simulations.(28,29)

A key ingredient of integral equations is the direct correlation function $c(1, 2)$. It is a member of a hierarchy of functions $c(1,..., s)$ whose leading terms $s=0$ and 1 are closely related by

$$c^{(0)} = -\beta\,\Delta A, \qquad c(1) = -\beta\,\Delta\mu_q \tag{1}$$

to the thermodynamic quantities ΔA and $\Delta\mu_q$, which play the leading role in the SPT and cluster integral approaches. Here the labels $i = 1, 2,...,$ are shorthand for the position $\mathbf{r}_i$, the orientation Ω_i, and species $q(i)$ of particle i. As usual, $\beta = 1/kT$.

In graphical expansion(30) $c(1,..., s)$ is the sum of all irreducible graphs on s labeled points (LPs) and some or no field points (FPs). With an FP i we associate a factor of ρ_q, the singlet density of species $q(i)$, and integration over $\mathbf{r}_i$ and Ω_i and summation over species $q(i)$. The LPs represent fixed particles and carry an associated factor 1. The bonds connecting points are f-bonds, defined below. Each graph occurs with a coefficient $1/\sigma$, where σ is the symmetry number. Irreducibility of a graph means the absence of articulation points (APs) and bridge points (BPs). APs and BPs are points whose deletion causes the graph to break into two or more fragments. If every fragment contains an LP, it is a BP; otherwise it is an AP.(30)

Much work has been done on the cavity function $y(1, 2)$, which results from considering pair correlations with the hard repulsion of the pair 1, 2 canceled, so that the cores can interpenetrate. For the case of one core engulfing the other, including the case of coincident hard cores represented by $y(1, 1)$, there is an explicit result in terms of the chemical potential of the engulfed species.(10,31–33) Unfortunately, this says little about integral equations, where $y(1, 2)$ for core overlap does not enter, except in a purely formal sense in the process of deriving the integral equations. With regard to integral equations, a more useful result would be one for $c(1, 1)$, which appears explicitly in the solutions. For the PY equation, there is a thermodynamic result for $c(1, 1)$, but this depends on the retention of only a restricted class of graphs. To date no such generally valid result for $c(1, 1)$ had been given for hard-core systems.

In the following I derive a general result for $c(1, 1)$ in multicomponent hard-particle fluids. Unlike the result for $y(1, 1)$, it is available only in graphical expansion, and it makes reference to the graphical expansion of $c(1)$. Its practical utility may be limited to use as a criterion for judging the suitability of integral equations. The latter question is of paramount interest for fluids of very long or flat shapes, i.e., nematogens, where our ignorance of what works is nearly total, and integral equation results for moderate elongations are just beginning to appear.(27) The result makes it possible to convert the density expansion of ΔA obtained by evaluation of the cluster integrals(16) directly into the density expansion of $c(1, 1)$.

2. FORMALISM

2.1. Bonding Functions

The calculation is based on the representation of correlation functions and related quantities by graphical expansions.(30) We use only density expansions, in which all graphs are free of APs. The pair potential $\phi(1, 2)$ appears in the bonds between pairs of graph points through the e-function and the Mayer f-function defined by

$$e(1, 2) = \exp[-\phi(1, 2)/kT], \qquad f(1, 2) = e(1, 2) - 1 \tag{2}$$

where k is Boltzmann's constant and T is the temperature. In the graphs we deal with, the bonds are f-bonds, represented by a solid line between points i and j to indicate a factor of $f(i, j)$. An e-bond between i and j, indicated by a dashed line, is the sum of the f-bonded and the unbonded states of the pair, i.e., indifference with respect to f-bonding. Unless e-bond is specified, the terms bond and bonding always refer to f-bonds. Similarly, AP, BP, connectedness, and irreducibility always refer to graphs with f-bonds.

For the sake of compact notation, I introduce some composite bonds consisting of several pair e-bonds. Capital letters appearing as arguments of functions are used to denote sets of points. I reserve the symbol S for the set of s LPs labeled 1,..., s. The symbol $E(S)$ stands for the product of all possible e-bonds in the set S:

$$E(S)=\prod_{1\leqslant i<j\leqslant s} e(i,j) \qquad \text{for} \quad s\geqslant 2 \tag{3}$$

Similarly, $E(W, X)$ stands for the product of all e-bonds going from a point in W to a point in X:

$$E(W,X)=\prod_{w\in W}\prod_{x\in X} e(w,x) \tag{4}$$

It is convenient to define two additional functions. By analogy with Eq. (2), define

$$F(W,X)=E(W,X)-1 \tag{5}$$

For sets X containing at least two points, also define the asymmetric function $G(W, X)$ by

$$G(W,X)=F(W,X)-\sum_{x\in X} F(W,x) \tag{6}$$

In terms of f-bonding, $E(W, X)$ contains all states of mutual bonding between the point sets W and X, while $F(W, X)$ contains all mutual bonding states with at least one bond. The bonding function $G(W, X)$ contains all bonding states such that *at least two points of X are bonded to W.* In the following applications, W is a set S of labeled points, which may be only a single point.

2.2. Composite Hard Cores

In the following I use the well-known special properties of hard-core interactions. Let $V(i)$ denote the space points included in the hard core of particle i. Then the e-function for a pair of particles interacting solely by hard-core repulsion is

$$e(1,2)=\begin{Bmatrix}1\\0\end{Bmatrix} \qquad \text{if} \quad V(1)\cap V(2)\begin{Bmatrix}=\\\neq\end{Bmatrix}\varnothing \tag{7}$$

where $\varnothing$ denotes the empty set. For the set of points W, we can define a composite hard core $V(W)$ by

$$V(W)=\bigcup_{w\in W} V(w) \tag{8}$$

which is the union of the hard cores of the particles in the set, whether or not there is hard-core overlap. Then the composite E-functions satisfy an equation analogous to Eq. (7), namely

$$E(W, X) = \begin{Bmatrix} 1 \\ 0 \end{Bmatrix} \quad \text{if} \quad V(W) \cap V(X) \begin{Bmatrix} = \\ \neq \end{Bmatrix} \varnothing \tag{9}$$

In the following we are concerned with the case where $W = S$, and the only core overlap is between one pair of S, labeled $s-1$ and s. Then we have

$$\frac{E(1,..., s)}{e(s-1, s)} = E(1,..., s-2, s-1 \cup s) \qquad \text{for} \quad V(s-1) \cap V(s) \neq \varnothing \tag{10}$$

Here $s-1 \cup s$ indicates a fused particle with a hard core $V(s-1) \cup V(s)$. In particular, if $V(s)$ is coincident with or contained in $V(s-1)$, then we have

$$\frac{E(1,..., s)}{e(s-1, s)} = E(1,..., s-1) \qquad \text{for} \quad V(s) \subset V(s-1) \tag{11}$$

where the subset symbol $\subset$ is defined to include the whole set or improper subset as one of the subsets. In the case at hand this corresponds to exact coincidence of two hard cores.

Similarly, the $E(S, X)$ satisfy

$$E(1,..., s; X) = E(1,..., s-2, s-1 \cup s; X) \qquad \text{for} \quad V(s-1) \cap V(s) \neq \varnothing \tag{12}$$

$$E(1,..., s; X) = E(1,..., s-1; X) \qquad \text{for} \quad V(s) \subset V(s-1) \tag{13}$$

2.3. Nonparallel Graphs and Correlation Functions

The analysis proceeds by considering the functions

$$n(S) = n(1,..., s) \tag{14}$$

defined as the sum of all nonparallel graphs on s LPs and one or more FPs. These graphs are defined by the requirements (a) there are no bonds between pairs of LPs, (b) there are no APs, (c) every FP can be reached from every other FP by a path of f-bonds and FPs without going through an LP. Requirement (c) may be restated as: the graph remains connected when all connections at the LPs are broken.

Denote the subset of irreducible graphs in $n(S)$ by $b(S)$ and the complementary set of reducible graphs by $q(S)$. For $s = 1$, bridge points cannot occur, and all graphs in $n(1)$ are irreducible, so that we have

$$n(1) = b(1) = c(1) \tag{15}$$

For $s=2$, the decomposition

$$n(1,2)=b(1,2)+q(1,2) \tag{16}$$

is needed in analyzing the direct correlation function $c(1,2)$. For $c(S)$ with $s \geqslant 3$, a further analysis of $q(S)$ in terms of the relation of BPs to the LPs is required. For $s=3$, such an analysis has been given in the course of deriving integral equations involving triplet correlations.(34) In the following I restrict the discussion to $c(1,2)$.

For subsequent manipulations and for the purpose of expressing the usual s-particle distribution functions in terms of the elementary graph function $n(S)$, it is convenient to introduce two further quantities, $z(S)$ and $z^*(S)$. We have

$$z(1)=n(1), \qquad z(1,2)=n(1,2)+n(1)+n(2) \tag{17}$$

$$\begin{aligned} z(1,2,3)=n(1,2,3)&+n(1,2)+n(1,3)+n(2,3) \\ &+n(1)+n(2)+n(3) \end{aligned} \tag{18}$$

and in general

$$z(S)=\sum_{\substack{H\subset S\\ H\neq\varnothing}} n(H) \tag{19}$$

The quantity $z^*(S)$ differs from $z(S)$ by exclusion of the $n(i)$. With $m(X)$ denoting the number of points in any point set X, we have

$$z^*(S)=\sum_{\substack{H\subset S\\ m(H)\geqslant 2}} n(H) \qquad \text{for} \quad m(S)\geqslant 2 \tag{20}$$

The expression for the s-particle distribution functions $g(1,..., s)$ in terms of the nonparallel graph functions is well known. In the present notation it is

$$g(S)=E(S)\exp z^*(S) \tag{21}$$

As a sum of graphs with f-bonds, $g(S)$ consists of all graphs such that every FP is connected to at least one LP, and every connected subgraph of LPs and FPs is free of APs. A subset of these graphs is the subset of connected graphs. A further subset of the latter one is the subset of irreducible graphs with s LPs. The set of all irreducible graphs with s LPs labeled $1,..., s$ is $c(1,..., s)$. Here we consider only $s=2$, where

$$g(1,2)=e(1,2)\,e^{n(1,2)} \tag{22}$$

The subset of irreducible graphs is then given by

$$c(1,2) = e(1,2)\, e^{n(1,2)} - 1 - q(1,2) \tag{23}$$

Although my primary aim is the derivation of an expression for $c(1,1)$, I begin by discussing the simpler problem of composite cores, engulfment, and coincidence for $z(S)$ and $n(S)$. This makes it possible to make contact with the known so-called zero-separation theorems(10,31–33) for the cavity function $y(1,2) = g(1,2)/e(1,2)$.

3. CONSTRUCTION FROM TREES

If one takes a graph in $n(S)$ and deletes the LPs $i = 1,..., s$ with all their attached f-bonds $f(i, x)$, where x is an FP, then one has left either a single FP or a connected graph Γ consisting of FPs and f-bonds. The original graph in $n(S)$ is defined as *belonging to* Γ. My task is an analysis of the reverse process. Starting with a connected graph Γ on FPs, I wish to construct the set of *all* graphs in $n(S)$ which belong to Γ, by adding f-bonds between Γ and the LPs. For the case $s = 2$, I also wish to carry out such a construction for the irreducible subset of graphs, $b(1,2)$. Note that Γ and the LPs are distinguishable by their labelings, so that combinatorial problems do not arise. Given Γ with its correct coefficient $1/\sigma$, all graphs in $n(S)$ are obtained by taking all acceptable ways of adding f-bonds from $E(S, \Gamma)$. The conditions that must be met for the graph in $n(S)$ are (a) every LP must be bonded to Γ, and (b) there must be no APs. The prescription for meeting these conditions requires a preliminary discussion of the structure of the connected graphs on FPs.

3.1. Structure of Star-Trees

The set of connected graphs on FPs consists of the subset of irreducible graphs or *stars*, and the set of *trees of stars* connected by sharing APs. Since I focus almost entirely on the connectivity, I refer to the connected graphs on FPs synonymously as the set of *star-trees*, including the stars as *improper trees*, and referring to the trees of two or more stars as *proper trees*.

In the following it becomes essential to classify the component stars of a proper star-tree by the number of APs they contain. A star which contains n APs is called an *n-star*. The n-stars with $n \geq 2$ are classified as *inner stars*, while 1-stars are synonymously called *outer stars* of a proper star-tree. It will emerge that 1-stars and 2-stars play a special role in the analysis. Improper trees may be included in the classification as 0-stars.

The symbols A and B are reserved to denote the set of points in a 1-star and 2-star, respectively. An added prime indicates that the AP(s) is to be omitted. Thus, A'_k stands for the set of points in the kth 1-star with its single AP omitted. While A'_k contains at least one point, B'_k may be empty. The latter situation occurs when B_k consists of two points connected by an f-bond.

I use Y to denote the set of points in an improper tree and T to denote the points of a proper tree. For a proper tree T, U is the subset of points *not* contained in outer stars, each of the latter taken without its AP. Thus,

$$U = T - \sum_k A'_k \tag{24}$$

where the sum runs over all outer stars.

3.2. Bonding Functions $L_n(S, Y)$ and $L_n(S, T)$

For a given tree Y or T, $L_n(S, Y)$ or $L_n(S, T)$ is the sum of all products of f-bonds connecting S with Y or T such that we produce a graph in $n(S)$. Similarly, one can define bonding functions for the irreducible graph sum $b(S)$ and for $z(S)$. My primary interest here is in $b(1, 2)$. However, I begin with the easier problem of $n(S)$, which makes it possible to obtain results which imply the known zero-separation theorems.(10,31–33)

The bonding functions for $n(S)$ require every LP in S to be bonded to the tree. For this reason, it is simpler to consider first $z(S)$, which allows unbounded LPs. Graphs in $z(S)$ consists of some or no unbonded LPs and a single connected graph free of APs. Thus, the added bonds from S to the tree must fulfill the single requirement that no APs remain in the connected graphs with $t \leqslant s$ LPs. There are three cases.

For the single point p, one needs simply at least one f-bond from p to an LP, so that

$$L_z(S, p) = F(S, p) \tag{25}$$

For a star Y, at least two points of Y must be bonded to LPs, so that

$$L_z(S, Y) = G(S, Y) \tag{26}$$

For a proper tree T, each outer star must be bonded to an LP by at least one point other than its AP α in order to destroy the role of α as an AP. Once this is done, no APs remain, so that there is indifference to bonding of any other points in T. Indifference with respect to bonding of a point x is reflected in a factor $E(S, x)$, so that

$$L_z(S, T) = E(S, U) \prod_k F(S, A'_k) \tag{27}$$

From this result for $z(S)$, it is easy to deduce the corresponding results for $n(S)$. The inversion of Eq. (19) is a well-known combinatorial problem with the solution

$$n(S) = \sum_{\substack{H \subset S \\ H \neq \varnothing}} (-1)^{m(S-H)} z(H) \tag{28}$$

From this it follows immediately that

$$L_n(S, Q) = \sum_{\substack{H \subset S \\ H \neq \varnothing}} (-1)^{m(S-H)} L_z(S, Q) \qquad \text{for} \quad Q = p,\, Y, \text{or } T \tag{29}$$

3.3. Core Overlap Theorems

In the partial results for $L_z(S, Q)$, as given in Eqs. (25)–(27), the bonds from the LPs occur solely in the form of $E(S, X)$, with $X = p$, Y, U, A'_k, or $a \in A'_k$. Therefore, Eqs. (12) and (13) for composite cores apply unchanged to $z(S)$, and we obtain the results

$$z(1,..., s) = z(1,..., s-1 \cup s) \qquad \text{for} \quad V(s-1) \cap V(s) \neq \varnothing \tag{30}$$

$$z(1,..., s) = z(1,..., s-1) \qquad \text{for} \quad V(s) \subset V(s-1) \tag{31}$$

The corresponding result for $n(S)$ is obtained by using the inversion formula (29) and grouping terms according to whether they contain both $s-1$ and s, only $s-1$, only s, or neither. For overlap of $V(s-1)$ and $V(s)$ the result is

$$n(1,..., s) = n(1,..., s-1 \cup s) - n(1,..., s-1) - n(1,..., s-2, s)$$
$$\text{for} \quad V(s-1) \cap V(s) \neq \varnothing \tag{32}$$

For the special case of $V(s)$ engulfing or coincident with $V(s-1)$ this reduces to

$$n(1,..., s) = -n(1,..., s-1) \qquad \text{for} \quad V(s-1) \subset V(s) \tag{33}$$

Note that the roles of the two partners in the engulfment pair are opposite in $z(S)$ and $n(S)$. In the case of $z(S)$, only the *engulfing* core is effective, in the case of $n(S)$ it is the *engulfed* core.

Similar results for $g(1,..., s)/e(s-1, s)$ follow by the use of Eqs. (10), (21), and

$$z^*(1,..., s) = z(1,..., s) - \sum_{i=1}^{s} z(i) \tag{34}$$

I quote only the result for engulfment or coincidence. Then

$$\frac{g(1,..., s)}{e(s-1, s)} = g(1,..., s-1)\, e^{-z(s)} \qquad \text{for} \quad V() \subset V(s-1) \tag{35}$$

This is the familiar result$^{(10,31-33)}$ in terms of the configurational chemical potential of species $q(s)$, when one recalls that

$$z(1) = c(1) = -\beta\, \Delta\mu_{q(1)} \tag{36}$$

3.4. Bonding Functions and Pseudographs

Equations (31) and (33) for engulfment or coincidence have a simple interpretation in terms of what I call pseudographs. Consider each $E(S, X)$ as a product of $e(i, x)$ and each $e(i, x)$ expressed in terms of f-bonds by Eq. (2). For engulfment or coincidence the relevant product of f's is

$$f(s-1, x)\, f(s, x) = -f(s-1, x) \qquad \text{for} \quad V(s-1) \subset V(s) \tag{37}$$

If one treats the product on the left-hand side as the legitimate f-bond on the right-hand side, then $z(S)$ and $n(S)$ have pseudographical expansions in which one LP of the engulfment pair is ineffective in the sense of having no incident f-bonds, while all incident f-bonds refer to the core of the surviving partner. When Eq. (37) applies, the pseudographical expansions of $n(1,..., s)$ and $z(1,..., s)$ look just like the graphical expansions of $-n(1,..., s-1)$ and $z(1,..., s-2, s)$.

The functions $n(S)$ lead to a particularly simple result, because only connectedness and absence of APs are demanded. When we go to subsets of $n(S)$ with conditions involving the BPs, then the situation is much more complicated. The simplest case is $s=2$, where the only subset to be considered is $b(1, 2)$, the set of irreducible graphs in $n(1, 2)$. Even here, the general case of engulfment leads to the appearance of pseudographs with *both* types of f-bonds, i.e., referring to $V(1)$ and $V(2)$. For this reason, I consider only the simplest case, *coincidence of two identical hard cores.*

When 1 and 2 have identical cores, only one type of f-bond enters the LP $1=2$ for the coincident configuration. We then have an expansion of

$b(1, 1)$ in pseudographs which look like graphs in $b(1)$ but occur with a coefficient which differs from the proper coefficient $1/\sigma$. Define

$$R_b = \text{ratio of coefficient of pseudograph in } b(1, 1) \text{ to coefficient of corresponding graph in } b(1) \tag{38}$$

For the ratio R_n, defined in an analogous fashion for $n(1, 1)$ and $n(1)$, we have $R_n = -1$ for *all* graphs in $n(1)$. We shall see that R_b depends on topological properties of the tree to which the graph in $b(1)$ belongs. For this reason, the coincidence theorem for $b(1, 1)$ is available only in graphical expansion.

The coincidence theorem for $c(1, 2)$ is expressed in terms of a ratio R_c, defined as in Eq. (38) with $c(1, 1)$ and $c(1)$ replacing $b(1, 1)$ and $b(1)$. The ratio R_c is related simply to R_b. From Eq. (23) we have for coincidence of cores

$$c(1, 1) = -1 - q(1, 1) = -1 - n(1, 1) + b(1, 1) \tag{39}$$

If we use $n(1, 1) = -n(1) = -c(1)$, this becomes

$$c(1, 1) = -1 + c(1) + b(1, 1) \tag{40}$$

Since $c(1) = b(1)$, this means that we have simply

$$R_c = R_b + 1 \tag{41}$$

In $c(1, 1)$ there are two terms independent of R_b. The leading term in the density expansion is contributed by $f(1, 2)$, which yields $f(1, 1) = -1$. The linear term in densities comes from the triangle of f-bonds on LPs 1 and 2 and one FP, with coefficient 1. For $1 = 2$, we have $f(1, 1) = -1$ and $f(13) f(12) = -f(13)$, so that we obtain the leading term in $c(1)$, a single f-bond connecting 1 and the FP, with the correct coefficient 1. Here $R_c = 1$, because there is no contribution from R_b, since graphs in $b(1, 2)$ require at least *two* FPs. For all higher orders in the densities, R_b makes a nonzero contribution to R_c.

4. COINCIDENCE THEOREM FOR $b(1, 2)$ AND $c(1, 2)$

4.1. Calculation of R_b

We proceed by constructing the bonding function $L_b(1, 2; Y)$ and $L_b(1, 2; T)$ and comparing the case of $1 = 2$ with $L_b(1, Y)$ and $L_b(2, Y)$.

The latter two quantities are obtained by specializing $L_z(1, Y)$ and $L_z(1, T)$ to $S=1$:

$$L_b(1, Y) = G(1, Y) \tag{42}$$

$$L_b(1, T) = E(1, U) \prod_k F(1, A'_k) \tag{43}$$

I consider first a set of topologically equivalent bondings from 1, and then construct the set of all bondings from 2 such that only the irreducible graphs in $b(1, 2)$ are produced. For improper trees the calculation is very simple. The LP 1 must be bonded to at least two points of Y; the sum of all such bondings is $G(1, Y)$. The same applies to the LP 2, resulting in a factor $G(2, Y)$. The result of evaluating the product in the limit $V(1) = V(2)$ is

$$G(1, Y)\, G(2, Y)|_{1=2} = -G(1, Y) + \sum_{\substack{x \in Y \\ y \in Y \\ x \neq y}} f(1, x) f(1, y) \tag{44}$$

In the sum, each pair occurs twice, compared to once in $G(1, Y)$. Therefore we may rewrite Eq. (44) as

$$L_b(1, 1; Y) = -L_b(1, Y) + 2 \sum_{\substack{\text{pairs}(x, y) \\ x, y \in Y}} f(1, x) f(1, y) \tag{45}$$

This provides the answer for R_b in the case of an improper tree Y. The pseudographs in $b(1, 1)$ occur with a factor of -1 relative to the corresponding graphs in $b(1)$, except for minimally, i.e., doubly LP-bonded graphs, which have $-1+2=1$. Thus,

$$R_b = \begin{cases} 1 & \text{if } Y \text{ is minimally LP-bonded} \\ -1 & \text{otherwise} \end{cases} \tag{46}$$

For proper trees T a much longer calculation is required. First one must define a set of topologically equivalent bondings from 1. After adding two or more bonds from 1 to T, one forms a new graph $T(1)$. In $T(1)$, a certain part of T, denoted by T_1, is irreducibly bonded to 1. In other words, the LP 1, T_1, and the bonds connecting them form a star, which is denoted by $T_1(1)$. The subtree T_1 is either a single component-star of T, a connected subtree of T, or all of T. *An equivalent set of bondings is one that produces the same* T_1. Any connected subtree of T can be made into T_1; the set of all bondings that does so is $L_b(1, T_1)$, as determined by the status of the component stars in T_1, *not* in T.

The second step of the calculation, where one constructs all bondings from 2 that produce irreducible graphs, depends on the status of the star

$T_1(1)$ in the star-tree $T(1)$. One must distinguish the three possible cases (1) $T_1(1)$ is an inner star of $T(1)$, (2) $T_1(1)$ is all of $T(1)$, and (3) $T_1(1)$ is an outer star of $T(1)$.

Case 1 is easily disposed of. The bonding from 1 to T_1 contains at least two f-bonds from 1 to T_1. But since T_1 is part of an *inner* star of $T(1)$, the reducibility or irreducibility of a graph is indifferent to the bonding from 2 to T_1. Therefore, the bonding from 2 contains a factor $E(2, T_1)$, which is incompatible with the bonding from 1 to T_1 in the limit $1=2$, so that the product is zero. Therefore, *case 1 makes no contribution to* $L(1, 1; T)$.

Case 2 is relatively simple. The bonding from 1 to T is just $L_b(1, T)$. Since $T(1)$ is now a star, the set of all bondings from 2 to T is just $G(2, T)$. Evaluation of the product for $1=2$ leads to

$$L_b(1, T)\,G(2, T)|_{1=2} = -L_b(1, T) + E(U) \sum_{m} \prod_{k \neq m} F(1, A'_k) \sum_{a \in A'_m} f(1, a) \tag{47}$$

In the second term on the right, consider the ith term in the sum over m. It contains exactly all graphs in $L_b(1, T)$ such that the ith outer star is minimally, i.e., singly, bonded to the LP 1. Therefore, a graph with n singly bonded outer stars appears exactly n times in the sum over m. Therefore, the contribution of case 2 to R_b is exactly

$$-1 + N_1 \tag{48}$$

where N_1 is the number of minimally bonded outer stars. As implied by Eq. (47), only bonding from points other than the AP are counted in determining minimal bonding.

In case 3, $T_1(1)$ is an outer star of $T(1)$. This implies that T consists of two connected subtrees T_1 and T_2 which share a single AP, denoted by α. The sets of equivalent bondings from the LP 1 to T_1 depend on the status of component stars in T_1, rather than in T. When we break off T_2, it is possible to have reduction of an n-star in T to an $(n-1)$-star in T_1. This occurs when, out of m component stars attached to α, one goes into T_1, the other $m-1$ into T_2, so that α is no longer an AP in T_1. Only 0-stars and 1-stars play a special role in the bonding from 1. Therefore, we need to single out only the cases where $n-1=0$ or 1. In the light of this, case 3 must be broken down into (3a) one 1-star in $T \to$ 0-star in T_1, (3b) one 2-star in $T \to$ 1-star in T_1, (3c) neither of the above.

Case 3a occurs when 1 is bonded to a single outer star A_m of T. The set of all such bondings is $G(1, A_m)$. Note that in this case bonding to the AP of A_m is allowed. The bonding from 2 required to produce an irreducible graph is unaffected by the bonding from 1. Therefore, the sum of bondings from 2 is just $L_b(2, T)$. For $1=2$ this becomes

$$G(1, A_m)\, L_b(1, T)\big|_{1=2} = -L_b(1, T) + E(1, U) \prod_{k \neq m} F(1, A'_k) \sum_{a \in A'_m} f(1, a) \tag{49}$$

After summing over all outer stars of T, we obtain a contribution

$$-M_1 L_b(1, T) + E(1, U) \sum_m \prod_{k \neq m} F(1, A'_k) \sum_{a \in A'_m} f(1, a) \tag{50}$$

where M_1 is the number of outer stars in T. The second term in Eq. (50) is exactly the same as in case 2, Eq. (48). Therefore, the contribution of case 3a to R_b is

$$-M_1 + N_1 \tag{51}$$

Case 3b occurs when α, the AP between T_1 and T_2, is just an ordinary point, i.e., not an AP, in T_1. This star is denoted by B; it is a 2-star in T, but all attachments at α are broken off when T_2 is detached from T_1. The bondings from 1 which render $T_1(1)$ irreducible are given by the bonding function

$$L_b(1, T_1) = E(1, U_1 - B'')\, F(1, B'') \prod_{A_k \subset T_1} F(1, A'_k) \tag{52}$$

where

$$B'' = B' + \alpha, \qquad U_i = U \cap T_i \quad \text{for } i = 1, 2 \tag{53}$$

The sum of bondings from 2 that produce irreducible graphs is

$$E(2, U_2)\, F(2, T_1 - \alpha) \prod_{A_k \subset T_2} F(2, A'_k) \tag{54}$$

The product of the two factors in Eqs. (53) and (54) in the limit $1=2$ simplifies to

$$-L_1(1, T) + E(1, U - B') \prod_k F(1, A'_k) \tag{55}$$

where the product runs over all outer stars A'_k. The second term contains all graphs in $L_b(1, T)$ such that the special 2-star B is not LP-bonded, not counting bonding to the APs in B.

The result in Eq. (55) must be summed over all partitions of T into T_1 and T_2 such that a 2-star B in T is degraded into a 1-star in T_1. There is one such partition for each AP of each 2-star in T. Therefore, the number of such partitions, denoted by M_2, is twice the number of 2-stars in T. Upon summing over all 2-stars B_m in T, one obtains the following contribution to the bonding function $L_b(1, 1; T)$:

$$-M_2 L_b(1, T) + 2 \prod_k F(1, A'_k) \sum_m E(1, U - B'_m) \tag{56}$$

The ith term in the sum over m counts twice all graphs such that B'_i is not bonded to the LP 1. A graph with n unbonded 2-stars is counted $2n$ times. Therefore, the contribution of case 3b to R_b is

$$-M_2 + 2N_2 \tag{57}$$

where N_2 is the number of minimally LP-bonded, i.e., LP-unbonded, 2-stars.

The final case is 3c, where all 1-stars of T_1 are 1-stars in T. The set of bondings from 1 is given by the bonding function

$$L_b(1, T_1) = E(1, U_1) \prod_{A_k \subset T_1} F(1, A'_k) \tag{58}$$

The set of bondings from 2 such that an irreducible graph is produced is

$$E(2, U_2)\, F(2, T_1 - \alpha) \prod_{A_k \subset T_2} F(2, A'_k) \tag{59}$$

For $1 = 2$, the product of the two factors in Eqs. (58) and (59) is just

$$-L_b(1, T) \tag{60}$$

Such a term is obtained from each partition of a tree T into subtrees T_1 and T_2 subject to the condition (3c). Let this number be M_3. Then the contribution of case 3c to R_b is

$$-M_3 L_b(1, T) \tag{61}$$

In summing up the contributions to R_b from cases 1 through 3c, the M_i occur in the form

$$M = M_1 + M_2 + M_3 \tag{62}$$

All the M_i are numbers of partitions of the tree T into T_1 and T_2. Their sum exhausts all partitions of T into two nonempty subtrees. By adding up all contributions, we obtain the desired result

$$R_b = 2(N_1 + N_2) - (M + 1) \tag{63}$$

and as a consequence of Eq. (41),

$$R_c = 2(N_1 + N_2) - M \tag{64}$$

A formula which encompasses R_b for both proper trees T and stars Y is

$$R_b = 2N - (M+1) \tag{65}$$

where N is the number of minimally bonded n-stars for $n \leqslant 2$. In the case of a star Y, the number M of partitions is 0, and N is 1 for minimal bonding of Y, and 0 otherwise.

4.2. Range of Values of R_b and R_c

Before discussing the range of values that R_b can take on, it is of interest to note the special status of the component star consisting of two points connected by an f-bond. Since bonds to APs are not counted, this star is necessarily LP-unbonded when it occurs as a 2-star. Similarly, when it occurs as an outer star in T, it necessarily occurs minimally, i.e., singly LP-bonded in $b(1)$.

The formula (63) for R_b contains both positive and negative terms. The number of partitions M is obtained by summing partitions over APs. An m-AP is one with m attached stars. At an AP of multiplicity m, i.e., an m-AP, there are

$$M(\alpha) = 2^{m(\alpha)} - 2 \tag{66}$$

partitions of T into nonempty subtrees T_1 and T_2. Therefore we have

$$M = \sum_{\text{APs } \alpha} [2^{m(\alpha)} - 2] \tag{67}$$

It is easy to see that arbitrarily large values of M can be constructed without increasing N, so that there is no lower bound for R_b. On the other hand, additional minimally bonded 1-stars and 2-stars cannot be added without increasing the number of APs, so that we expect to have an upper bound on R_b. In the following we deduce it by building up more complex trees from simpler ones.

The simplest proper trees consist of a simple chain of $n \geqslant 2$ stars, connected at 2-APs. If all the stars are minimally bonded, then we have

$$N = n, \qquad M = 2(n-1), \qquad R_b = 2N - (M+1) = 1 \tag{68}$$

All other trees may be obtained from the simple chain by successive addition of component stars. In each step a new 1-star can be attached to the tree in one of two ways: (1) at a new 2-AP converted from an ordinary point of a component star, and (2) at an existing m-AP, converting it to an $(m+1)$-AP.

The algebraically largest change in one of these operations occurs when the added 1-star is minimally bonded to the LP. To find the largest R_b we need to consider only the minimally bonded case.

In operation 1, we gain $+2$ in $2N$ for adding an additional 1-bonded 1-star, and gain -2 in $-2M$ for adding an additional 2-AP. In addition, we have the change due to the change in status of the star with the new AP. This latter change is 0, except for the case in which the initial minimally LP-bonded 2-star becomes a 3-star, so that we gain -2 due to the loss of one minimally LP-bonded 2-star. Therefore, operation 1 results in a net change of 0 or -2.

In operation 2, we still gain $+2$ for an additional minimally LP-bonded 1-star. The change in $-M$ due to the number of partitions in converting one m-AP to an $(m+1)$-AP is

$$(2^m-2)-(2^{m+1}-2)=-2^m \tag{69}$$

Therefore, the net change in operation 2 is at most -2, for $m=2$.

It follows that the maximum value of R_b is 1, and this value occurs only for minimally LP-bonded stars and chains of minimally LP-bonded stars.

4.3. Explicit R_c

We have already noted that $R_c=1$ for the leading graph in $c(1)$. For all higher graphs, where R_b contributes, R_c is of the form

$$R_c=2-2L \tag{70}$$

where the nonnegative integer L is given by

$$L=-N+\sum_{\text{APs }\alpha}[2^{m(\alpha)-1}-1] \tag{71}$$

Figure 1 displays the graphs in $c(1)$ belonging to trees on two, three, and four points. In the reduced form of display the LP 1 and its attached bonds are omitted. Instead, the LP-bonded points of the tree are indicated by solid circles. The values of R_c are shown in a separate column. Through this order, the only values of R_c are 2 and 0. Negative values of R_c appear in the next order, with trees on five points.

Two standard approximations which may be compared are the PY and HNC integral equations. In these approximations $g(1,2)-c(1,2)$ is

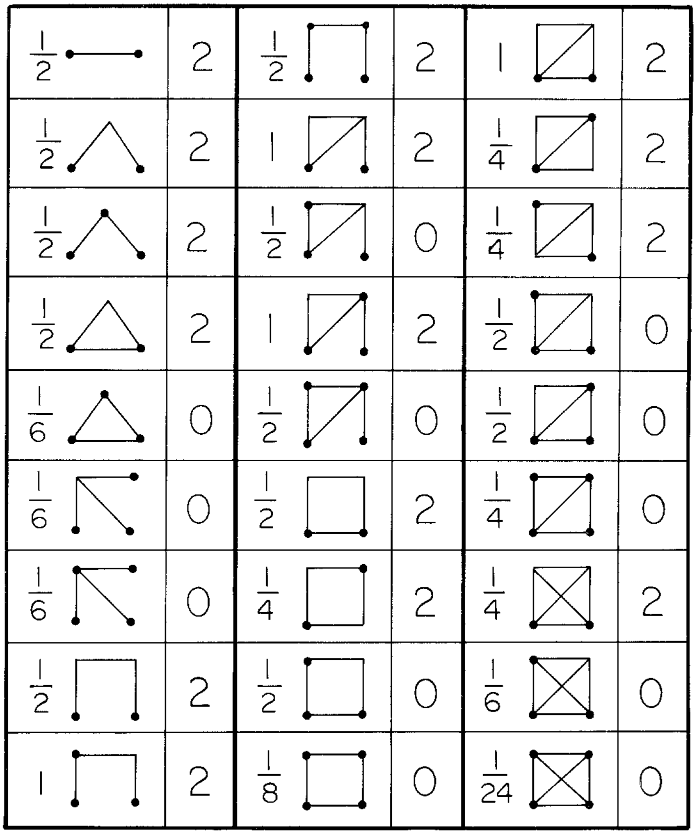

Fig. 1. Graphs in $c(1)$ with two, three, and four field points and their associated factors R_c. The LP 1 and its attached f-bonds are omitted; the LP-bonded field points are indicated by solid circles. The coefficient to the left of each graph is $1/\sigma$. The value to the right is R_c.

exact through graphs with two FPs for any pair interaction $\phi(1, 2)$. Because $g(1, 1) = 0$ whenever there is infinite repulsion for coincidence, $c(1, 1)$ is exact to the same order. However, for the purely hard interactions under consideration here, it is found that both integral equations are exact for $c(1, 1)$ through terms with *three* field points. This may be attributed to the occurrence of the factor $R_c = 0$ for the fully LP-bonded triangle in Fig. 1.

Figure 2 displays the errors committed by the PY and HNC equations in the lowest nonexact order of $c(1, 1)$, consisting of pseudographs with four FPs. In each case the omitted pseudographs can be summed into a single pseudograph by using e-bonds. The errors for the two approximations have opposite signs.

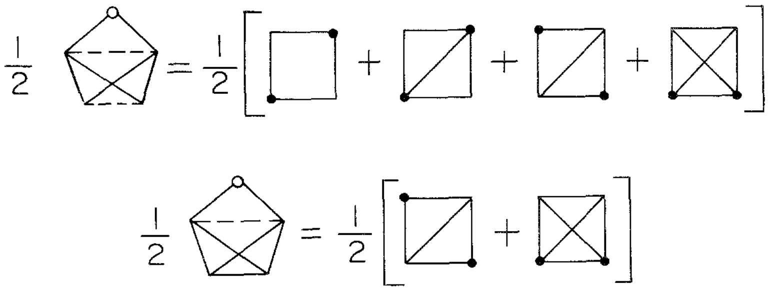

Fig. 2. The lowest order pseudographs omitted from $c(1, 1)$ in the PY (upper line) and HNC (lower line) equations. Individual pseudographs are given in the reduced form of Fig. 1; their sum is shown in full. The dashed lines are e-bonds.

A noteworthy feature of the PY approximation is the following: all pseudographs with two or more FPs in $c_{\mathrm{PY}}(1, 1)$ have $R_c = 2$, and occur with their correct coefficients $2/\sigma$. This can be seen from the characterization of the graphs in $c_{\mathrm{PY}}(1, 2)$. It contains all convex polygons whose vertices are the LPs 1 and 2 and all the FPs. All adjacent pairs on the periphery are mutually bonded; 1 and 2 are adjacent. All noncrossing sets of interior bonds are allowed. All of these graphs have symmetry number 1. Coalescing 1 and 2 produces pseudographs which correspond to graphs in $c(1)$; these satisfy the same conditions as the graphs in $c_{\mathrm{PY}}(1, 2)$ except for the presence of only one LP. Their symmetry number is 1 or 2. We count the number of graphs in $c_{\mathrm{PY}}(1, 2)$ that correspond to a given graph in $c(1)$, distinguishing the cases of coalescence and noncoalescence of f-bonds. Because of the prohibition against bond crossing, this amounts to counting the number of partitions of the ordered set of LP-bonded FPs on the periphery, going from 1 to 2. For m bonds from $1 = 2$, there are $m - 1$ such partitions in the case of noncoalescence, because the bonds on the periphery are uniquely assigned. For the case of coalescence, there are m such partitions, with a factor of -1 for the relation $f^2 = -f$. The total is $(m - 1) - m = -1$. There is an additional factor of -1 from $f(1, 1) = -1$. Finally, interchange of the labels 1 and 2 corresponds to distinct sets of graphs if $\sigma = 1$ in $c(1)$. For graphs in $c(1)$ with $\sigma = 2$, the corresponding graphs in $c(1, 2)$ are either invariant under the interchange or go into each other in pairs. Hence, we have $R_c = 2$ in both cases.

5. CONCLUSION

I have derived the coincidence theorem for $c(1, 2)$ for multicomponent hard-particle fluids. Only future calculations for fluids of nonspherical hard particles will make it possible to assess the utility of this result.

Some questions remain. First, it would be useful to have an analogous result for the Ree–Hoover graphs. While it is not difficult to do this explicitly in low order, it appears to be extraordinarily difficult to prove a *general* result for the Ree–Hoover graphs. Finally, can a fruitful connection be made with the overlap graph formalism used by Kratky(15)?

Generalization to hard cores with added attraction is ruled out in most cases, because the coalescence of two f-functions is not an f-function. The exception to this rule occurs for theories developed recently to deal with the case of site–site bonding.(35) Here multiple bonding of a site is forbidden, so that coalescence of two equivalent attraction bonds cannot occur for coincidence. In these cases, generalizations can be carried out.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under grants CHE-82 11236 and CHE-85 19759.

REFERENCES

1. L. Boltzmann, *Wissenschaftliche Abhandlungen* [Reprinted Chelsea, New York, 1968].
2. W. W. Wood and J. D. Jacobson, *J. Chem. Phys.* **27**:720 (1957).
3. T. E. Wainwright and B. J. Alder, AEC Report Contract No. W-7405-eng-48, Radiation Laboratory at Livermore, University of California; *Nuovo Cimento* **9** (Suppl. X):116 (1957).
4. H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**:369 (1959).
5. D. M. Tully-Smith and H. Reiss, *J. Chem. Phys.* **53**:4015 (1970); Erratum, **54**:3661 (1971).
6. J. J. Vieceli and H. Reiss, *J. Chem. Phys.* **57**:3746 (1973); *J. Stat. Phys.* **7**:143 (1973); **8**:299 (1973).
7. H. Reiss and R. V. Casberg, *J. Chem. Phys.* **61**:1107 (1974).
8. M. J. Mandell and H. Reiss, *J. Stat. Phys.* **13**:107, 113 (1975).
9. R. M. Gibbons, *Mol. Phys.* **17**:81 (1969).
10. B. Barboy and W. M. Gelbart, *J. Stat. Phys.* **22**:685 (1980), and references cited therein.
11. J. E. Kilpatrick, *Adv. Chem. Phys.* **20**:39 (1971).
12. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:939 (1964).
13. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **41**:1635 (1964).
14. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **46**:4181 (1967).
15. K. W. Kratky, *J. Stat. Phys.* **27**:533 (1982); **29**:129 (1982).
16. B. Mulder, Thesis, Utrecht (1986).
17. J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**:1 (1958).
18. J. M. van Leeuwen, J. Groeneveld, and J. deBoer, *Physica* **25**:792 (1959).
19. M. S. Green, *J. Chem. Phys.* **33**:1403 (1960).
20. E. Meeron, *J. Math. Phys.* **1**:192 (1960).
21. G. S. Rushbrooke, *Physica* **26**:1425 (1960).
22. T. Morita and K. Hiroike, *Prog. Theor. Phys.* **23**:1103 (1960).
23. L. Verlet, *Nuovo Cimento* **18**:77 (1960).
24. M. S. Wertheim, *Phys. Rev. Lett.* **10**:321 (1963); *J. Math. Phys.* **5**:643 (1964).

25. E. Thiele, *J. Chem. Phys.* **38**:1959 (1963).
26. M. Klein, *J. Chem. Phys.* **39**:1388 (1963).
27. A. Perera, P. G. Kusalik, and G. N. Patey, *J. Chem. Phys.* **87**:1295 (1987).
28. D. Frenkel and B. M. Mulder, *Mol. Phys.* **55**:1171, 1193 (1985).
29. J. W. Perram, M. S. Wertheim, J. L. Lebowitz, and G. O. Williams, *Chem. Phys. Lett.* **105**:277 (1984).
30. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964).
31. W. G. Hoover and J. C. Poirier, *J. Chem. Phys.* **37**:1041 (1962).
32. E. Meeron and A. J. Siegert, *J. Chem. Phys.* **48**:3139 (1968).
33. D. Henderson and E. W. Grundke, *Mol. Phys.* **24**:669 (1972).
34. M. S. Wertheim, *J. Math. Phys.* **8**:927 (1967).
35. M. S. Wertheim, *J. Stat. Phys.* **35**:19, 35 (1984); **42**:459, 477 (1986).